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EMISSION SPECTRUM OF THE NU3 BAND OF SF6 AT 1780 K.(U)

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Emission Spectrum of the ν_3 Band of SF_6 at 1780 K

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20 January 1978

Interim Report

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~~The author measured~~ the emission spectrum of the ν_3 band of SF_6 at 1780 K is measured in a shock tube. At this high temperature, the emission peaks at a frequency of 907/cm^{-1} (11.02 μ); at room temperature, the band has a peak intensity at 948/cm^{-1}. Lyman and Nowak observed similar but proportionately smaller shifts of the spectral maximum to lower frequencies at temperatures between 400 and 800 K. A knowledge of the high-temperature spectral distribution of

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20. ABSTRACT (Continued)

the ν_3 band is important for the design and interpretation of isotope separation experiments in which SF_6 is dissociated by selective multiphoton absorption of CO_2 laser photons.

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PREFACE

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EMISSION SPECTRUM OF THE ν_3 BAND OF SF_6 AT 1780 K

Studies of multiphoton dissociation of SF_6 in recent years[1-4] have stimulated interest in the ν_3 absorption band near 10.6 μm. Steinfield et al[5] and Petersen, Tiee, and Wittig[6] have observed that laser pumping of this band with a CO_2 laser induces absorption at lower frequencies. In shock tube experiments, Nowak and Lyman[7] measured the absorption spectrum of SF_6 at a number of CO_2 laser frequencies at temperatures between 400 and 1500 K. Their results show that the absorption coefficients for the laser lines P(12) through P(18) decrease monotonically with temperature above 300 K, whereas the absorption coefficients for P(20) through P(32) show a maximum before falling off with temperature. In Fig. 3 of the Nowak and Lyman work, the temperatures at which the absorption coefficient at each laser frequency goes through a maximum are plotted against frequency. These data are reproduced in Fig. 1 of the present paper as circles. We have examined the absorption spectra of Nowak and Lyman at several different temperatures and determined the frequency at which the spectral distribution is a maximum at each temperature. These data are plotted in Fig. 1 as squares.

We have measured the wavelength dependence of the SF_6 emission between 10 and 12 μ at a temperature of 1780 K and observed the shift of intensity to lower frequencies. The measurements were performed during shock tube studies of SF_6 dissociation[8] and reactions of H_2 and SF_6.[9] The initial conditions behind the incident shock wave were 1780 K, 0.93 atm, and 0.05% SF_6 diluted with argon. The emission was measured with a Santa Barbara Research Center mercury-germanium detector cooled with liquid helium and mounted on a Perkin-Elmer Model No. 99 prism monochromator. With a 2-mm-wide entrance slit, the monochromator had a triangular slit function with a full width at half maximum (FWHM) of 0.13 μ. The accuracy of the wavelength calibration is estimated to be ±0.05 μ.

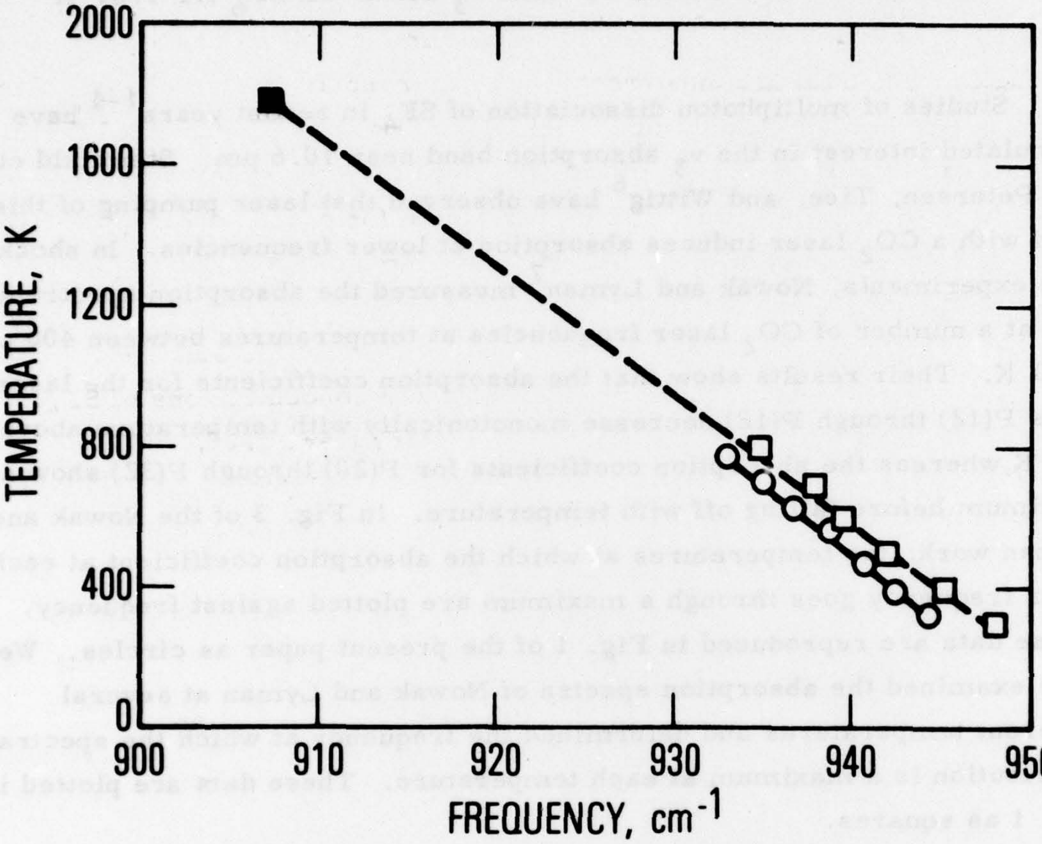

Figure 1. Temperatures (O) at Which Absorption Coefficients Are a Maximum (From Nowak and Lyman, Fig. 3) and Temperatures (□ ■) for Which the Spectral Distribution Is a Maximum at a Given Frequency. □, Nowak and Lyman; ■, present study.

The intensity jumped to a maximum behind the shock front and decayed as the SF_6 dissociated. In Fig. 2, the initial intensities are plotted against wavelength. The data are uncorrected for the monochromator slit function and spectral sensitivity variations. Schatz and Horning[10] measured the integrated band intensity, α_{STP}, of the 10.6-μ band at room temperature and found it to be 4800 cm^{-2} atm^{-1}. With this value for α_{STP}, the temperature and pressure conditions of the 0.05% SF_6 experiments, and the 16.5-cm shock tube diameter, we estimated the self-absorption of the data of Fig. 2 to be about 13% at the peak intensity of 11.0 μ. To test for self-absorption at 11.0 μ, we conducted two experiments at lower concentrations of SF_6. The signals normalized with the SF_6 concentration were 1.00, 1.08, and 1.18 for 0.05% SF_6, 0.025% SF_6, and 0.0125% SF_6 mixtures, respectively. If we consider the measurements to have a relative accuracy of about ±5%, they agree with the estimate of 13% self-absorption.

In Fig. 2, the uncorrected emission spectrum is shown to peak at 11.02 ± 0.10 μ (907 ± 8 cm^{-1}) with a FWHM of approximately 0.58 μ (48 cm^{-1}). This frequency of the peak has been plotted in Fig. 1 at 1780 K and falls close to a linear extrapolation of the temperatures and frequencies estimated from the data of Nowak and Lyman.[7] The present, low-resolution data show no structure. However, the large density of states at this temperature makes any significant structure unlikely. The data of Nowak and Lyman showed progressively less structure with temperature. The frequency of the maximum in the absorption spectrum is shifted approximately $2.7 \times 10^{-2} cm^{-1}/°K$.

Plotted against temperature in Fig. 3 are spectral bandwidths (FWHM) estimated from the present data and from the data of Nowak and Lyman.[7] Corrections to the spectral profile of Fig. 2 reduce the bandwidth ~8% for the slit width and 6% for the self-absorption; the corrected bandwidth is therefore 42 ± 6 cm^{-1}. At low temperatures, the ν_3 spectrum[11] resolves into separate P, Q, and R branches and cannot be characterized by a single

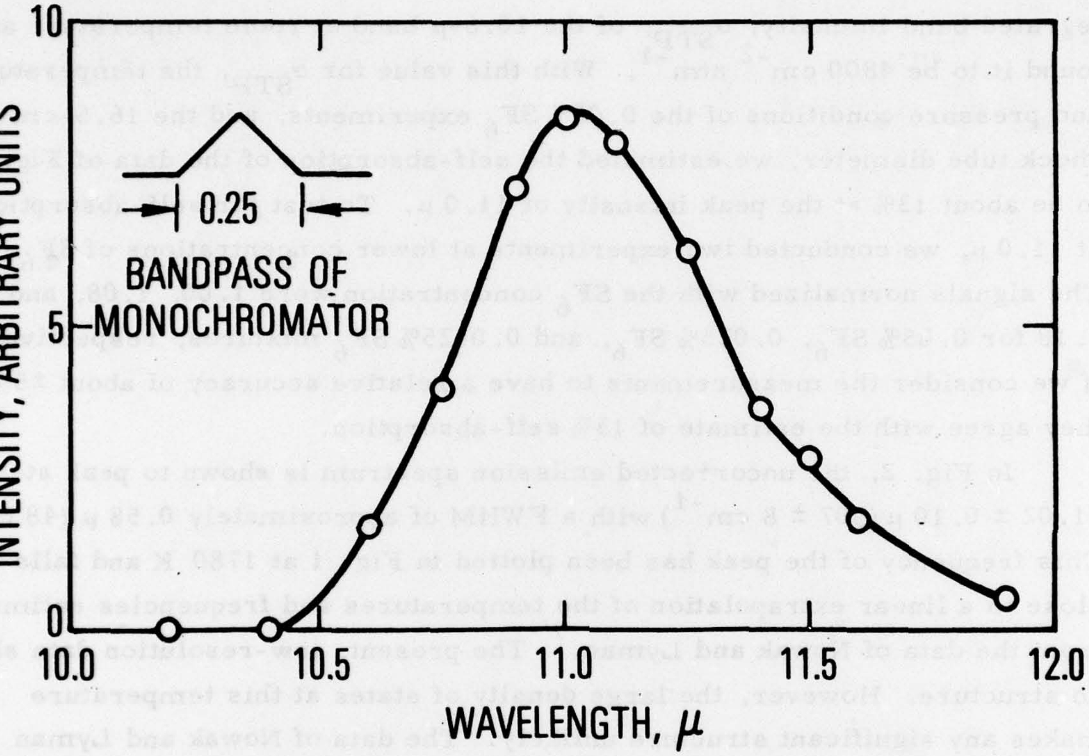

Figure 2. Emission of ν_3 Band of SF_6 at 1780 K

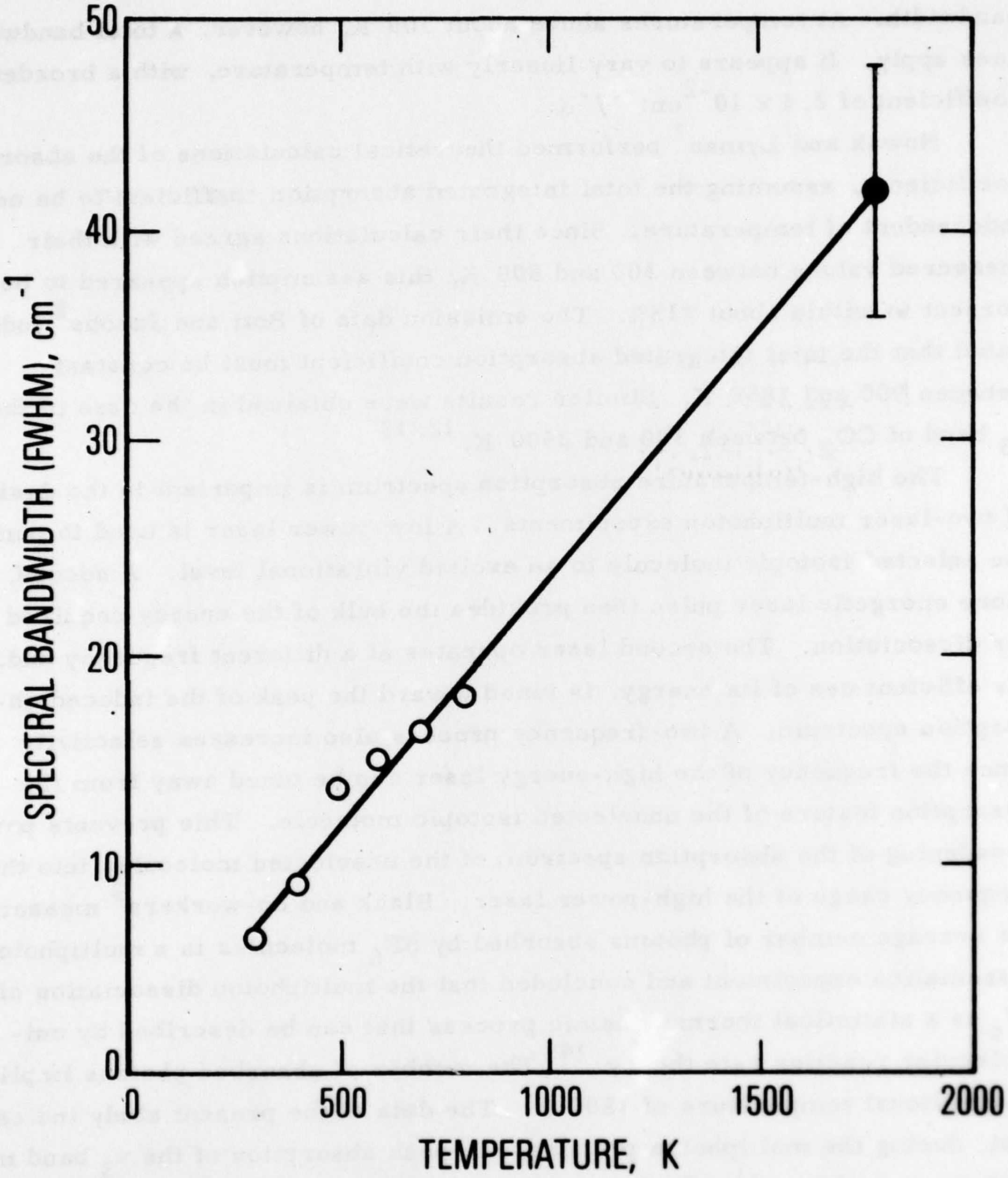

Figure 3. **Bandwidth (FWHM) of ν_3 Band of SF_6. O, absorption data of Nowak and Lyman; ●, emission data of present study.**

bandwidth. At temperatures above about 300°K, however, a total bandwidth does apply. It appears to vary linearly with temperature, with a broadening coefficient of $2.4 \times 10^{-2} cm^{-1}/°K$.

Nowak and Lyman[7] performed theoretical calculations of the absorption coefficients, assuming the total integrated absorption coefficient to be nearly independent of temperature. Since their calculations agreed with their measured values between 300 and 800°K, this assumption appeared to be correct to within about ±15%. The emission data of Bott and Jacobs[8] indicated that the total integrated absorption coefficient must be constant between 900 and 1850 K. Similar results were obtained in the case of the ν_3 band of CO_2 between 300 and 2500 K.[12, 13]

The high-temperature absorption spectrum is important in the design of two-laser multiphoton experiments. A low-power laser is used to pump the selected isotopic molecule to an excited vibrational level. A second, more energetic laser pulse then provides the bulk of the energy required for dissociation. The second laser operates at a different frequency and, for efficient use of its energy, is tuned toward the peak of the induced absorption spectrum. A two-frequency process also increases selectivity since the frequency of the high-energy laser can be tuned away from the absorption feature of the unselected isotopic molecule. This prevents power broadening of the absorption spectrum of the unselected molecules into the frequency range of the high-power laser. Black and co-workers[3] measured the average number of photons absorbed by SF_6 molecules in a multiphoton dissociation experiment and concluded that the multiphoton dissociation of SF_6 is a statistical thermodynamic process that can be described by unimolecular reaction rate theory.[14] The number of absorbed photons implied a vibrational temperature of 1800 K. The data of the present study indicate that, during the multiphoton process, the peak absorption of the ν_3 band may shift by up to 40 cm^{-1}. Shifts are indicated by Stafast, Schmid, and Kompa,[15] who measured effective absorption cross sections for several laser lines at various energy densities.

In conclusion, the spectral profile of the ν_3 band of SF_6 appears to be shifted linearly with temperature to lower frequencies, and the structureless spectral profile can be described with a half-width that is also linear with temperature. The present emission measurements are consistent with laser absorption measurements[7] at lower temperatures. Such emission measurements may prove useful in planning two-frequency multiphoton experiments for SF_6 and other molecules. Emission measurements have the advantage of not being restricted to laser frequencies. Similarly, quantitative emission or absorption measurements at the shifted frequencies during multiphoton dissociation experiments could provide data for comparison with theoretical predictions.

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